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NONAQUEOUS ELECTROLYTE SOLUTION SECONDARY BATTERY

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## Specification

**(54) [Title of the Invention]**

Nonaqueous electrolytic solution secondary battery

**(57) [Abstract]**

[Purpose] A nonaqueous electrolyte solution secondary battery that utilizes a positive electrode with a specific composition, wherein deterioration in the electrolyte solution based on decomposition of the solvent is controlled and the cycle characteristic is improved.

[Means of solution] A nonaqueous electrolyte solution secondary battery that utilizes a positive electrode shown in  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$  (Wherein, M is an element selected from among the group consisting of Mn, B, Mg, Al, Si, Ca, Ti, V, Fe, Cu, Zn and Ga, and at the same time,  $0 \leq a \leq 1.2$ ,  $0.01 \leq b \leq 0.4$ ,  $0.01 \leq c \leq 0.4$  and  $0.02 \leq b+c \leq 0.5$ ), the solute is a electrolyte salt selected from either of  $\text{LiN}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$  or  $\text{LiC}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_2(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$  (Wherein, n=1 to 5, m=1 to 5, but n and m cannot both be 1 at the same time), and furthermore, a 5-member or 6-member heterocyclic compound containing at least one among oxygen, sulfur, or nitrogen as a component of the ring structure is included in the solvent.

**[Claims of the invention]**

[Claim 1] In a nonaqueous electrolyte solution secondary battery having a positive electrode shown in  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$  {(Wherein, M is at least one type of element selected among the group of manganese (Mn), boron (B), magnesium (Mg), aluminum (Al), silicon (Si), calcium (Ca), titanium (Ti), vanadium (V), iron (Fe), copper (Cu), zinc (Zn) and gallium (Ga), and at the same time,  $0 \leq a \leq 1.2$ ,  $0.01 \leq b \leq 0.4$ ,  $0.01 \leq c \leq 0.4$  and  $0.02 \leq b+c \leq 0.5$ }, a negative electrode made of a lithium metal or a material mainly comprising one that is capable of storing and releasing lithium, a separator that isolates the above-mentioned two electrodes, and a nonaqueous electrolyte solution comprising a solvent and a solute, which nonaqueous electrolyte solution

secondary battery is characterized by the fact that the aforementioned solute is a electrolyte salt selected from either of  $\text{LiN}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$  or  $\text{LiC}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_2(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$  (Wherein, n=1 to 5, m=1 to 5, but n and m cannot 1 at the same time), and furthermore, the above-mentioned solvent includes a 5-member or 6-member heterocyclic compound containing at least one among oxygen, sulfur, or nitrogen as a component of the ring structure.

[Claim 2] The nonaqueous electrolyte solution secondary battery described in claim 1, in which 0.01 to 3.0 moles/l of the aforementioned heterocyclic compound is included for the aforementioned nonaqueous electrolyte solution.

[Claim 3] The nonaqueous electrolyte solution secondary battery described in claim 1 in which the aforementioned electrolyte salt is  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$  or  $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$ .

[Claim 4] The nonaqueous electrolyte solution secondary battery described in claim 1, in which the aforementioned nonaqueous electrolyte solution includes 0.5 to 2.0 moles/l of the aforementioned electrolyte salt.

[Detailed description of the invention]

[0001]

[Field of industrial application] The present invention pertains to an nonaqueous electrolyte solution secondary battery, and the invention further pertains to an improvement in the nonaqueous electrolyte solution in order to improve cycle characteristics.

[0002]

[Prior art] When propylene carbonate, etc. are used as an electrolyte solution solvent of nonaqueous electrolyte solution secondary battery, stability and cycle characteristics of the electrolyte solution are sharply reduced due to decomposition of the solvent molecules. In order to improve the above-mentioned problems, an aromatic carbonate is added (see Japanese Kokai [Unexamined] Patent Application No. Hei 8-2737 -- for reference) for an improvement in stability of the electrolyte solution.

[0003] However, according to the study performed by the present inventors, a high capacity can be achieved but an adequate cycle characteristic cannot be achieved when a lithium transition metal composite oxide shown in the following general formula  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$  (Wherein, M is at least one element selected from the group consisting of Mn, B, Mg, Al, Ca, Ti, V, Fe, Cu, Zn and Ga, and at the same time,  $0 \leq a \leq 1.2$ ,  $0.01 \leq b \leq 0.4$ ,  $0.01 \leq c \leq 0.4$  and  $0.02 \leq b+c \leq 0.5$ ) is used as a positive electrode even when an aromatic carbonate is included.

[0004]

[Problems to be solved by the invention] Based on the above background, the purpose of the present invention is to eliminate the above-mentioned existing problems, and to produce a nonaqueous electrolyte solution secondary battery with a superior cycle characteristic compared to nonaqueous electrolyte solution secondary batteries of the prior art.

[0005]

[Means to solve the problem] In order to achieve the above-mentioned purpose, the present invention is a nonaqueous electrolyte solution secondary battery characterized by the fact that the

solute is a electrolyte salt selected from either of  $\text{LiN}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$  or  $\text{LiC}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_2(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$  (Wherein, n=1 to 5, m=1 to 5, but n and m are not 1 at the same time), and furthermore, the above-mentioned solvent includes a 5-member or 6-member heterocyclic compound containing at least one of oxygen, sulfur, or nitrogen as a component of the ring structure in a nonaqueous electrolyte solution secondary battery having a positive electrode of  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$  {(Wherein, M is at least one element selected from the group consisting of manganese (Mn), boron (B), magnesium (Mg), aluminum (Al), silicon (Si), calcium (Ca), titanium (Ti), vanadium (V), iron (Fe), copper (Cu), zinc (Zn) and gallium (Ga), and at the same time,  $0 \leq a \leq 1.2$ ,  $0.01 \leq b \leq 0.4$ ,  $0.01 \leq c \leq 0.4$  and  $0.02 \leq b+c \leq 0.5$ }, a negative electrode made of a lithium metal or a material mainly comprising a material capable of storing and releasing lithium, a separator that isolates the above-mentioned two electrodes, and a nonaqueous electrolyte solution comprised of a solvent and a solute. Based on the above-mentioned structure, reduction in the charge capacity at the time of the charge-discharge cycle of the nonaqueous electrolyte solution secondary batteries of the prior art can be controlled.

[0006] In other words, a 5-member or 6-member heterocyclic compound containing at least one oxygen, sulfur, or nitrogen as a ring structural component is added to a nonaqueous electrolyte solution secondary battery to increase the ion conductivity, and at the same time, a stable and high-quality film is formed on the surface of the negative electrode to prevent contact between the negative electrode and solvent molecules, and deterioration in the nonaqueous electrolyte solution is prevented. Furthermore, decomposition reaction of the electrolyte solution that take place at the time of charge-discharge and reversibility at the time of charge-discharge is increased.

[0007] Furthermore, in the battery of the present invention, an electrolyte salt shown in  $\text{LiN}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$  or  $\text{LiC}(\text{C}_n\text{F}_{2n+1}\text{SO}_2)_2(\text{C}_m\text{F}_{2m+1}\text{SO}_2)$  (Wherein, n=1 to 5, m=1 to 5, but n and m cannot both be 1 at the same time) is added to the nonaqueous electrolyte solution and used so as to form a high-quality film based on a stable anion on the surface of the positive

electrode. In this manner, charge transfer from the positive electrode and diffusion of lithium ion from the positive electrode to lithium ion in solution is smoothly accomplished, and deterioration in the crystalline structure of the positive electrode is prevented.

[0008] For specific examples of the 5-member or 6-member heterocyclic compounds containing at least one oxygen, sulfur, or nitrogen as a structural component of the ring used in the present invention, 1,3-propane sultone (5-member heterocyclic compound containing oxygen and sulfur as ring structural components), sulfolane (5-member heterocyclic compound containing oxygen and sulfur as ring structural components), butadiene sulfone (5-member heterocyclic compound containing oxygen and sulfur as ring structural components), isoxazole (5-member heterocyclic compound containing oxygen and nitrogen as ring structural components), N-methyl morpholine (6-member heterocyclic compound containing oxygen and nitrogen as ring structural components), N-methyl-2-pyrrolidone (5-member heterocyclic compound containing oxygen and nitrogen as ring structural components), etc. can be mentioned.

[0009] The target effect can be achieved when a small amount of the above-mentioned heterocyclic compound is added to the nonaqueous electrolyte solution, and an amount in the range of 0.01 to 3.0 moles/l is further desirable.

[0010] The present invention pertains to an improvement in the additive for the nonaqueous electrolyte solution. Thus, conventional materials commonly used for nonaqueous electrolyte solution secondary battery can be used without any restrictions in the present invention as well.

[0011] For examples of the solvent used for the nonaqueous electrolyte solution, organic solvents such as ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC), mixed solvents of the above-mentioned organic solvents with a low-boiling point solvents such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and methyl ethyl carbonate (EMC) can be mentioned.

[0012] An especially desirable solvent having good affinity with the additive specified in the present invention and having good cycle characteristics is a mixed solvent of one or more of the

cyclization carbonates and one or more linear carbonates with a volume ratio of 1:4 to 4:1.

[0013] Furthermore, for a negative electrode, metal lithium, lithium alloys such as lithium-aluminum alloy, lithium-lead alloy, and lithium tin alloy, graphite, coke, carbonate materials such as sintered materials, and metal oxides having a lower potential than those of positive electrode active materials such as SnO<sub>2</sub>, SnO, TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>3</sub>.

[0014]

[Embodiment of the invention] In the following, the present invention is explained in further detail with working examples, but the present invention is not limited to the working examples shown below, and furthermore, modifications within the range of the invention are possible.

[0015] <Test 1> In Test 1 shown below, the relationship between the composition ratio of the complex oxide (positive material) and charge-discharge cycle characteristics was evaluated.

[0016] [Production of positive electrode] Mixing was performed for lithium hydroxide (LiOH), nickel hydroxide (Ni(OH)<sub>2</sub>), cobalt hydroxide (Co(OH)<sub>2</sub>) and manganese dioxide (MnO<sub>2</sub>) in a mortar at the molar ratio shown in Table I below to give the starting raw material for the positive electrode. A heat-treatment was performed for the above mixture for 20 hours at a temperature of 750°C, and pulverization was further performed to produce a composite oxide. The composite oxide produced above was used as the positive electrode active material, and mixing was performed for 90 parts by weight of the powder of the above-mentioned positive electrode, 5 parts by weight of synthetic graphite powder, and N-methyl-2-pyrrolidone (NMP) solution of 5 parts by weight of polyvinylidene fluoride to produce a slurry. The above slurry was coated onto both surfaces of an aluminum foil by the doctor blade method to form an active material layer and vacuum drying was further performed for 2 hours at a temperature of 150°C to produce a positive electrode.

[0017] [Production of negative electrode] Mixing was performed for 95 parts by weight of natural graphite and an NMR solution of 5 parts by weight polyvinylidene fluoride to produce a slurry. The above-mentioned slurry was coated onto both surfaces of a copper foil by a doctor

blade method to form a carbon layer and vacuum drying was further performed for 2 hours at a temperature of 150°C to produce a negative electrode.

[0018] [Production of nonaqueous electrolyte solution] 1.0 moles/l of LiN(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) was dissolved in an equal volume of a solution of ethylene carbonate and dimethyl carbonate, then, vinylene carbonate was further added to the resulting solution as a specific heterocyclic compound so as to form 1.5 moles/l for the nonaqueous electrolyte solution and mixing was performed to produce a nonaqueous electrolyte solution.

[0019] [Production of battery] With the above-mentioned positive electrode, negative electrode and nonaqueous electrolyte solution produced, production of a nonaqueous electrolyte solution secondary battery (battery size: diameter of 14 mm, height of 50 mm) of AA size was carried out. In this case, a porous film made of polypropylene was used as a separator in each battery.

[0020] In this case, 9 types of batteries of A1 to A9 of the present invention where a positive electrode of general formula Li<sub>a</sub>CobM<sub>c</sub>Ni<sub>1-b-c</sub>O<sub>2</sub> (Wherein, M is at least one element selected from the group consisting of Mn, B, Mg, Al, Ca, Ti, V, Fe, Cu, Zn and Ga, and at the same time, 0≤a≤1.2, 0.01≤b≤0.4, 0.01≤c≤0.4 and 0.02≤b+c≤0.5) and 7 types of batteries of V1 to V7 for comparison having compositions outside the range of the above-mentioned composition, a total of 16 different batteries were prepared.

[0021] Furthermore, charge-discharge cycle testing was performed for the above-mentioned batteries. In the charge-discharge cycle test, 1 cycle consists of charging each battery at room temperature (25°C) under 200 mA at a constant current, then, discharging under 200 mA at a constant current to 4.2 V, and the cycle was repeatedly performed, and the number of cycles until the discharge capacity is 90% or below of the initial discharge capacity was obtained. And the results obtained are shown in Table I below.

[0022]

[Table I]

Battery	Molar ratio of each element in composite oxide				Number of Cycles (number)
	Li	Ni	Co	Mn	
Battery A1	1.00	0.98	0.01	0.01	328
Battery A2	1.00	0.79	0.01	0.20	335
Battery A3	1.00	0.59	0.01	0.40	343
Battery A4	1.00	0.50	0.10	0.40	332
Battery A5	1.00	0.79	0.20	0.01	333
Battery A6	1.00	0.60	0.20	0.20	332
Battery A7	1.00	0.50	0.20	0.30	330
Battery A8	1.00	0.59	0.40	0.01	328
Battery A9	1.00	0.50	0.40	0.10	334
Battery V1	1.00	0.50	0.45	0.05	162
Battery V2	1.00	0.50	0.05	0.45	160
Battery V3	1.00	0.45	0.15	0.40	163
Battery V4	1.00	0.45	0.40	0.15	165
Battery V5	1.00	0.90	0.00	0.10	106
Battery V6	1.00	0.90	0.10	0.00	113
Battery V7	1.00	1.00	0.00	0.00	60

[0023] As shown in Table I, superior cycle characteristics were achieved in composite oxides A1 to A9 shown in structural formula of  $\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$  ( $0 \leq a \leq 1.2$ ,  $0.01 \leq b \leq 0.4$ ,  $0.01 \leq c \leq 0.4$  and  $0.02 \leq b+c \leq 0.5$ ) in comparison to comparison batteries V1 to V7.

[0024] In test 1 above, the case where vinylene carbonate was used as the 5-member or 6-member heterocyclic compound containing at least one of oxygen, sulfur, or nitrogen as a ring structural component, and the number of cycle is likely to be increased when a material other than vinylene carbonate is used, for example, 1,3-propane sultone, sulfolane, butadiene sulfone,

isoxazole, N-methyl morpholine or N-methyl-2-pyrrolidone is used.

[0025] <Test 2> In test 2 shown below, the relationship between the starting raw material of composite oxide used as the positive electrode and the charge-discharge cycle characteristics of the battery was examined.

[0026] To prepare the starting raw material, mixing was performed for lithium hydroxide ( $\text{LiOH}$ ), nickel hydroxide ( $\text{Ni(OH)}_2$ ), cobalt hydroxide ( $\text{Co(OH)}_2$ ) and raw materials shown in Table II below in a mortar in such a manner that the molar ratio of each element of  $\text{Li:Ni:Co:M}$  ( $\text{Li, Ni, Co elements other than above}$ ) = 1:0.6:0.3:0.1 could be achieved. Furthermore, a heat-treatment was performed for the above-mentioned mixture for 20 hours at a temperature of 750°C, and pulverization was further performed to produce a composite oxide.

[0027] The composite oxide produced above was used as the positive electrode active material, and production of batteries B1 to B12 was performed as in the case of battery A1 above. Then, the cycle test was performed as described above. And the results obtained are shown in Table II below.

[Table II]

Battery	Starting raw material other than LiOH, Ni(OH) <sub>2</sub> and Co(OH) <sub>2</sub>	Number of Cycles (number)
Battery B1	H <sub>3</sub> BO <sub>3</sub>	333
Battery B2	Mg(OH) <sub>2</sub>	331
Battery B3	Al(OH) <sub>3</sub>	345
Battery B4	SiO	310
Battery B5	Ca(OH) <sub>2</sub>	328
Battery B6	Ti(OH) <sub>4</sub>	333
Battery B7	V <sub>2</sub> O <sub>6</sub>	334
Battery B8	FeOOH	342
Battery B9	Cu(OH) <sub>2</sub>	331
Battery B10	ZnO	333
Battery B11	Ga <sub>2</sub> O <sub>3</sub>	332
Battery B12	MnO <sub>2</sub>	336

[0029] As shown in Table II, excellent cycle characteristics can be achieved when a composite oxide shown in structural formula of Li<sub>a</sub>Co<sub>b</sub>M<sub>c</sub>Ni<sub>1-b-c</sub>O<sub>2</sub> (Wherein, M is at least one type of element selected from the group consisting of Mn, B, Mg, Al, Ca, Ti, V, Fe, Cu, Zn and Ga, and at the same time, 0≤a≤1.2, 0.01≤b≤0.4, 0.01≤c≤0.4 and 0.02≤b+c≤0.5) is used.

[0030] In test 2 above, the case where vinylene carbonate was used as the ring structural component, and the number of cycles is likely to be increased when a material other than vinylene carbonate is used, for example, 1,3-propane sultone, sulfolane, butadiene sulfone, isoxazole, N-methyl morpholine or N-methyl-2- pyrrolidone is used.

[0031] <Test 3> In test 3 shown below, the relationship between the type of electrolyte salt and the cycle characteristics of the battery was examined.

[0032] First, as a starting raw material, mixing was performed for LiOH, Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub> and MnO<sub>2</sub> in a mortar in such a manner that a molar ratio of each element of Li:Ni:Co:Mn = 1:0.6:0.3:0.1 was achieved. Furthermore, a heat-treatment was performed for the above-mentioned mixture for 20 hours at a temperature of 750°C, and pulverization was further performed to produce a composite oxide.

[0033] 1.0 moles/l of electrolyte salt was dissolved in a solution comprising equal volumes of ethylene carbonate and dimethyl carbonate, then, vinylene carbonate was further added to the solution as a heterocyclic compound so as to form 1.5 moles/l for the nonaqueous electrolyte solution and mixing was performed to produce a nonaqueous electrolyte solution.

[0034] The composite oxide and nonaqueous electrolyte solution produced above were used and production of batteries of the present invention C1 to C6 and comparison batteries W1 to W6 was performed as in the case of test 1 above.

[0035] Then, the cycle test was performed as described above. And the results obtained are shown in Table III below.

[Table III]

Battery	Electrolyte salts	Number of cycles (number)
Battery C1	LiN(CF <sub>3</sub> SO <sub>2</sub> )(C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> )	335
Battery C2	LiN(C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> ) <sub>2</sub>	322
Battery C3	LiN(C <sub>2</sub> F <sub>5</sub> SO <sub>2</sub> ) <sub>2</sub>	331
Battery C4	LiC(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> (C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> )	320
Battery C5	LiC(CF <sub>3</sub> SO <sub>2</sub> )(C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> ) <sub>2</sub>	324
Battery C6	LiC(C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> ) <sub>3</sub>	329
Battery V1	LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	287
Battery V2	LiC(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub>	294
Battery V3	LiPF <sub>6</sub>	226
Battery V4	LiBF <sub>4</sub>	204
Battery V5	LiClO <sub>4</sub>	216
Battery V6	None	197

[0037] As shown in Table III, excellent cycle characteristics were achieved in battery C1 and battery C2. This indicates LiN(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub> or LiN(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) can be used effectively as the electrolyte salt.

[0038] Furthermore, cycle characteristics of comparison batteries W1 and W2 wherein LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> or LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub> is used are likely to be inferior. In this case, n=1 and m=1 in the structural formula LiN(C<sub>n</sub>F<sub>2n+1</sub>SO<sub>2</sub>)(C<sub>m</sub>F<sub>2m+1</sub>SO<sub>2</sub>) or LiC(C<sub>n</sub>F<sub>2n+1</sub>SO<sub>2</sub>)<sub>2</sub>(C<sub>m</sub>F<sub>2m+1</sub>SO<sub>2</sub>). It is hypothesized that the LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> or LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub> dissolved the positive electrode aluminum foil used as the current collector and deterioration in the electrode was accelerated.

[0039] <Test 4> In test 4 shown below, the relationship between the type of 5-member or 6-member heterocyclic compound containing at least one of oxygen, sulfur, and nitrogen and the cycle characteristic of the battery was examined.

[0040] In this case, the composite oxide produced in test 4 [sic] above was used as the positive

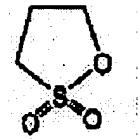
electrode. Furthermore, 1.0 mole/l of LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) was dissolved in an equal volume solution of ethylene carbonate and dimethyl carbonate, and then, a variety of heterocyclic compounds were added to the above-mentioned solution so as to form 1.5 moles/l for the nonaqueous electrolyte solution and mixing was performed to produce a nonaqueous electrolyte solution.

[0041] The composite oxides and nonaqueous electrolyte solution produced as described above was used and production of batteries of the present invention D1 to D7 was performed as in the case of test 1.

[0042] Furthermore, the structural formula of 1,3-propane sultone used as a heterocyclic compound in battery D1 of the present invention is shown as chemical formula 1 below.

[0043]

[Chemical formula 1]



1,3-propane sultone

[0044] Also, the structural formula of sulfolane used as a heterocyclic compound in battery D2 of the present invention is shown as chemical formula 2 below.

[0045]

[Chemical formula 2]



sulfolane

[0046] The structural formula of butadiene sulfone used as a heterocyclic compound in battery D3 of the present invention is shown as chemical formula 3 below.

[0047]

[Chemical formula 3]

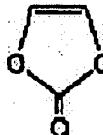


butadiene sulfone

[0048] Furthermore, the structural formula of vinylene carbonate used as a heterocyclic compound in battery D4 of the present invention is shown as chemical formula 4 below.

[0049]

[Chemical formula 4]

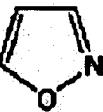


Vinylene carbonate

[0050] The structural formula of isoxazole used as a heterocyclic compound in battery D5 of the present invention is shown as chemical formula 5 below.

[0051]

[Chemical formula 5]

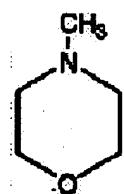


isoxazole

[0052] The structural formula of N-methyl morpholine used as a heterocyclic compound in battery D6 of the present invention is shown as chemical formula 6 below.

[0053]

[Chemical formula 6]

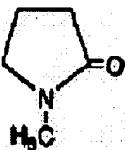


N-methyl morpholine

[0054] Furthermore, the structural formula of N-methyl-2- pyrrolidone used as a heterocyclic compound in battery D7 of the present invention is shown as chemical formula 7 below.

[0055]

[Chemical formula 7]



N-methyl-2-pyrrolidone

[0056] Furthermore, comparison battery X was produced as in the case of battery D1 above without a heterocyclic compound.

[0057] For each battery produced, the above-mentioned cycle test was performed as in the case of test 1. And the results obtained are shown in Table IV. It should be noted that the results for battery C1 transferred from Table III are shown in Table IV as well.

[0058]

[Table IV]

Battery	Heterocyclic compound	Number of cycles (number)
Battery D1	1,3-propane sultone	310
Battery D2	Sulfolane	312
Battery D3	Butadiene sulfone	332
Battery D4 (C1)	Vinylene carbonate	335
Battery D5	Isoxazole	330
Battery D6	N-methyl morpholine	318
Battery D7	N-methyl-2-pyrrolidone	315
Battery X	None	204

[0059] As shown in Table IV, the batteries of the present invention D1 to D7 exhibit far superior cycle characteristics compared to those of comparison battery X. In this case, the 5-member or 6-member heterocyclic compound containing at least one of oxygen, sulfur, or nitrogen and forms a high-quality and stable film over the negative electrode and prevents contact between the negative electrode and solvent molecules, and as a result, decomposition of the electrolyte solution is controlled and reversibility at the time of charge-discharge is increased.

[0060] Furthermore, exceptionally superior cycle characteristics are observed in batteries D3 to D5 containing a heterocyclic compound having an unsaturated bond in the ring structure, and in this case, the film-forming reaction is promoted by the unsaturated bond included in the compound.

[0061] In test 4 above, the case where  $\text{LiCo}_{0.6}\text{Mn}_{0.3}\text{Ni}_{0.1}\text{O}_2$  is used as the positive electrode material, but an increase in the cycle characteristic is observed when a positive electrode having a different composition shown in the structural formula

$\text{Li}_a\text{Co}_b\text{M}_c\text{Ni}_{1-b-c}\text{O}_2$  (Wherein,  $0 \leq a \leq 1.2$ ,  $0.01 \leq b \leq 0.4$ ,  $0.01 \leq c \leq 0.4$  and  $0.02 \leq b+c \leq 0.5$ , and M is at

least one element selected from the group consisting of Mn, B, Mg, Al, Ca, Ti, V, Fe, Cu, Zn and Ga) is used as well.

[0062] <Test 5> In test 5 shown below, an examination was done to determine a suitable amount of the above-mentioned heterocyclic compound added to the nonaqueous electrolyte solution.

[0063] First, mixing was performed for 1.5 moles/l of LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) with an equal volume mixed solvent comprised of ethylene carbonate and dimethyl carbonate to produce a solution. For the above-mentioned solution produced, vinylene carbonate was added as a heterocyclic compound at the concentration shown in Table V and production of a nonaqueous electrolyte solution was performed.

[0064] Production of batteries E1 to E7 was performed with the above-mentioned nonaqueous electrolyte solution produced as in the case of battery A1 above. And furthermore, a comparison battery Y was produced without vinylene carbonate.

[0065] Then, the cycle test was performed for each battery produced as in the case of test 1. The results obtained are shown in Table V below. It should be noted that the results for battery C1 transferred from Table III are shown in Table IV as well.

[0066]

[Table V]

Battery	Amount of vinylene carbonate added (moles/l)	Number of cycles (number)
Battery E1	0.001	312
Battery E2	0.01	324
Battery E3	0.1	329
Battery E4 (C1)	1.5	335
Battery E5	3.0	324
Battery E6	4.0	318
Battery E7	5.0	312
Comparison battery Y	None	175

[0067] As shown in Table V, exceptionally good cycle characteristics were observed for batteries E2 to E5. Based on the results obtained, it is desirable to use 0.01 to 3.0 moles/l of vinylene carbonate for the nonaqueous electrolyte solution. In this case, when the amount of vinylene carbonate is 30 moles/l or above, a reduction in the cycle characteristic is observed, and it is hypothesized that the electrode reaction is inhibited in this case as an excess amount of vinylene carbonate results in decomposition on the positive electrode.

[0068] A separate test further confirmed that the amount of 0.01 to 3.0 moles/l was suitable when a heterocyclic compound other than vinylene carbonate was used.

[0069] <Test 6> In test 6 shown below, an examination was done to determine a suitable amount of the electrolyte salt added to the nonaqueous electrolyte solution.

[0070] First, 1.0 moles/l of vinylene carbonate was dissolved in an equal volume mixed solvent composed of ethylene carbonate and dimethyl carbonate to produce a solution. To the above-mentioned solution, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) was added as an electrolyte salt at the

concentration shown in Table VI and production of a nonaqueous electrolyte solution was achieved.

[0071] Production of batteries F1 to F8 was done with the above-mentioned nonaqueous electrolyte solutions produced as in the case of battery A1 above.

[0072] Then, the cycle test was performed for each battery as in the case of test 1. The results obtained are shown in Table VI below. It should be noted that the results of battery C1, which is F4 of the present invention, and the results of W6 transferred from Table III are shown in Table IV as well.

[0066]

[Table VI]

Battery	Amount of LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> (C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> ) (moles/l)	Number of Cycles (number)
Battery F1	0.001	309
Battery F2	0.01	312
Battery F3	0.5	320
Battery F4 (C1)	0.1	329
Battery F5	1.0	335
Battery F6	2.0	320
Battery F7	3.0	313
Battery F8	4.0	305
Comparison battery W6	None	197

[0074] As shown in Table VI, exceptionally good cycle characteristics were observed in batteries F3 to F6. Based on the results obtained, it is desirable to use 0.5 to 1.0 mole of LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>) for the nonaqueous electrolyte solution.

[0075] In this case also, a separate test further confirmed that the amount of 0.5 to 2.0 moles/l was suitable when LiN(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub> was used as an electrolyte.

[0076]

[Effect of the invention] As explained in detail above, the ion conductivity in the electrolyte solution can be increased and deterioration of nonaqueous electrolyte solution caused by decomposition of the solvent in the nonaqueous electrolyte solution can be prevented and a nonaqueous electrolyte solution secondary battery with a good cycle characteristic can be produced when a nonaqueous electrolyte solution secondary battery containing a specific additive and specific electrolyte salt is used, and the contribution of the present invention to industry is significant.